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<b>14. ABSTRACT</b> <p>In this work, we explore novel approaches to new polymers the poly(butyne-1,4-diyl). These are synthesized from 1,2,3-butatrienes, highly unsaturated monomers. Tetrasubstituted systems bearing bulky aliphatic substituents can be polymerized under controlled conditions. The tetramethyl system cannot be controlled. Using diphenyl substituents, we have developed a new approach to the synthesis of soluble polyacetylenes. Using 1,4-diphenylsubstituted butatrienes, we polymerize these monomers to form a non-conjugated poly(1,4-diphenyl-2-butyne-1,4-diyl). This soluble, processable materials can be converted to the conjugated (poly(diphenylacetylen-alt-acetylene) for through the application of strong protic bases. We provide synthesis procedures and characterization of both the precursor and final polymers.</p>					
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## Final Technical Report

The work performed for this program constitutes the doctoral thesis of Dr. Ashebir Fiseha. It is summarized below as abstracts and/or experimental procedures and the reference to the publication is given. Additionally there was a theoretical paper by Dr. Pollack, the Pi and his colleague, Dr. Vernon Morris, on the mechanism of the polymerization.

V. P. Morris and S.K. Pollack, The Singlet-Triplet Gap in 1,2,3-Butatriene and Its Consequences on the Mechanism of its Spontaneous Polymerization , *J. Phys. Chem B.*, **102(26)**, 5042-5046 (1998).

The reactivity of 1,2,3 butatriene,  $C_4H_4$ , has been postulated to be due to the presence of low-lying triplet states. However, there have been no experimental or theoretical determinations of the energy separations or geometries of these states. We have examined the structures, energetics, and possible mechanisms involved in the self-polymerization of the title compound using single-determinant *ab initio* molecular orbital theory. We find that the magnitude of the singlet-triplet gap for the monomer and its relatively high positive heat of formation does not allow for a mechanism involving the direct formation of an isolated triplet species. We speculate on an alternative mechanism and show its relationship to recent work on related reactive monomers.

S.K. Pollack, A. Fiseha and B. Narayanswami, Butatriene-Based Polymer Chemistry. 2. Synthesis and Characterization of Poly[1,1,4,4-bis(pentamethylene)1,2,3-butatriene], *Macromolecules*, **30(18)**,5265,1997.

The cumulene 1,1,4,4-bis(pentamethylene)butatriene has been shown to undergo a thermally induced 1,4 free-radical polymerization to yield a crystalline polymer with a unique non-conjugated acetylene containing backbone. This polymerization occurs in both the melt and in solution. Typical free-radical inhibitors prevent the thermally induced polymerization. The reaction occurs in the presence or absence of free-radical initiators. The polymer is crystalline with a triclinic unit cell ( $a=9.87\text{\AA}$ ,  $b=6.10\text{\AA}$ ,  $c=4.97\text{\AA}$ ,  $\alpha=113.7^\circ$ ,  $\beta=85.2^\circ$ ,  $\gamma=100.6^\circ$ ). No melting or glass transition are observed via differential calorimetry, but an irreversible exothermic transition is observed from both solution and melt polymerized material. This is interpreted as a cold crystallization process. Trapping of the polymerizing monomer with TEMPO leads to soluble oligomers.

**Synthesis of pentamethylene allenic phosphonate(1):** Under a dry nitrogen atmosphere, 2g (16.1 mmol) of 1-ethynyl-1-cyclohexanol in 30 mL of dry dichloromethane was added dropwise to a stirred mixture of 4.4g (28.2 mmol) of diethylchlorophosphite and 3.47g (43.4 mmol) of freshly distilled pyridine. The resulting mixture was stirred for 48 h. The reaction was followed by IR and was complete after 48 h. The solvent was removed by rotary evaporator under reduced pressure. The product (5.1 g) was dissolved in 35 mL of THF and the suspension was added dropwise to 100 mL of stirring 8:1 mixture of THF and water at  $0^\circ\text{C}$ . After stirring at room temperature for 1 h the product was extracted several times with diethyl ether, dried over anhydrous magnesium sulfate, filtered

and the solvent was removed by rotary evaporator. The product was purified by column chromatography using florisil (100-200 mesh, Fisher). After purification, the allenic phosphonate was an oil and the yield is 81 %.  $^1\text{H}$  NMR 1.33 (t,  $J=7.0$  Hz, 6 H,  $2^*-\text{CH}_3$ ), 1.5-1.7 (m, 6 H,  $-(\text{CH}_2)_3-$ ), 2.19 (q,  $J=3.4$  Hz, 4 H,  $-(\text{CH}_2)_2\text{C}=\text{C}=\text{C}-$ ), 4.1 (m, 4 H,  $-\text{OCH}_2\text{CH}_3$ ), and 5.18 ppm (b, d, 1 H,  $-\text{C}=\text{C}=\text{CH}-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) : 15.9, 16.1 ( $-\text{OCH}_2\text{CH}_3$ ); 25.4, 26.5, 29.6 ( $-(\text{CH}_2)_5-$ ); 61.4, 61.7 ( $-\text{OCH}_2\text{CH}_3$ ); 78.8 ( $-\text{C}=\text{C}=\text{CH}$ ); 103 ( $\text{C}=\text{C}=\text{CH}$ ); 128.2 ppm ( $-\text{C}=\text{C}=\text{CH}$ ). IR (cast from  $\text{CDCl}_3$ ) : 2985, 2930, 2854; 1958 ( $\text{C}=\text{C}=\text{C}$ ); 1444, 1259  $\text{cm}^{-1}$ . MS : 244 (40,  $\text{M}=\text{C}_{12}\text{H}_{21}\text{PO}_3$ ), 216 (22,  $\text{M}-\text{C}_2\text{H}_4$ ), 188 (89), 171 (71), 135 (100), 105 (75), 91 (82), 81 (76), 65 (63).

**Synthesis of 1,1,4,4-Bis(pentamethylene-1,2,3-Butatriene) (BPMB, 2):** Under a dry nitrogen atmosphere, 2.6 mL (4.2 mmol) of *n*-butyllithium was added dropwise (over 10 m) to a stirred mixture of freshly distilled diisopropylamine in 20 mL of dry THF at  $-78^\circ\text{C}$  to form lithium diisopropylamide (LDA) in situ. The yellow solution was warmed to room temperature for 30 m and then cooled to  $-78^\circ\text{C}$  and 0.94 mL (4 mmol) of **1** added dropwise over 10 m followed immediately by 0.5 mL (4.8 mmol) of cyclohexanone. The mixture was stirred at room temperature for 16 h. Solvent removal via rotary evaporator (2h, rt) left a viscous yellow oil. The product was purified by column chromatography (under nitrogen using florisil as stationary phase and petroleum ether (degassed for several hours) as an eluent).  $^1\text{H}$  NMR 1.43 (b, m, 10 H,  $-(\text{CH}_2)_3-$ ), 2.07 ppm ( $(\text{CH}_2)_2\text{C}=\text{C}=\text{C}-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) : 26.1, 27.7, 34.9 ( $-(\text{CH}_2)_5-$ ); 116 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ); 151 ppm ( $-\text{C}=\text{C}=\text{C}=\text{C}-$ ). IR (cast from  $\text{CDCl}_3$ ) : 2940, 2852, 2875 ( $-(\text{CH}_2)_5-$ ); 1650 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ); 1434  $\text{cm}^{-1}$  ( $\text{CH}_2$  bend). MS : 188 (64,  $\text{M}=\text{C}_{14}\text{H}_{20}$ ), 159 (6,  $\text{M}-\text{C}_2\text{H}_4$ ), 131 (30), 105 (22), 91 (100), 65 (21).

### Synthesis of the homopolymer of BPMB

Monomer **2** (4 mmol, 0.752g) was dissolved in 20 mL of freshly distilled benzene in a pressure tube. To this as added 65.6 mg (0.4 mmol) of AIBN initiator. This solution was subjected to five freeze-pump-thaw cycles and the tube was then sealed under vacuum. The polymerization was carried out in a temperature controlled oven at 60°C for 48h. At the end of this period, the insoluble polymer was isolated by filtration and vacuum-drying to gave 0.331g (44.0%) of the polymer. Raman (acetylenic) 2221,2204 cm<sup>-1</sup>.

### Diradical Trapping Experiments

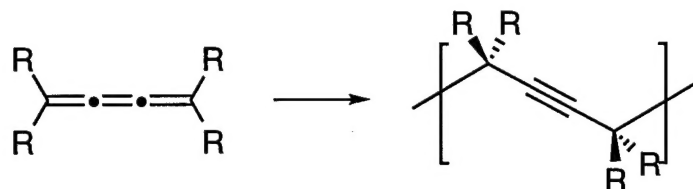
63 mg (0.4 mmol) of TEMPO (2,2,6,6-tetramethyl-1-piperidinoxy) in 8 mL of toluene was placed in a sealable tube, degassed (freeze-thaw-pump) several times and kept under nitrogen atmosphere. The solution was cooled to -78°C and 36 mg (0.19 mmol) of BPMB was added. The tube was then sealed and the mixture was warmed to room temperature and allowed to stand for 4 days. The solution was then added to acetonitrile, but no precipitation was observed. Removal of the solvent on a rotatory evaporator yielded an oily product which after 4 hours solidified to a low melting solid (26% yeild). (for peak labeling, see below) <sup>1</sup>H NMR(CDCl<sub>3</sub>) 1-1.17 (s, **Me**); 1.17-1.37 (b, s, **β**); 1.43-1.90 (b,multiplet, **3,4,δ,δ'**); 1.95-2.29 (**γ, γ'**). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (for assignments, see below). IR (neat) 2210,2240 cm<sup>-1</sup> (acetylenic)

S. K. Pollack and Ashebir Fiseha , Butatriene-Based Polymer Chemistry 3: A New Route to Substituted Poly(acetylene)s Through the Rearrangement of Poly(2-butyne-1,4-diyl)s, *Macromolecules*, 31(6),2002-2006(1998).

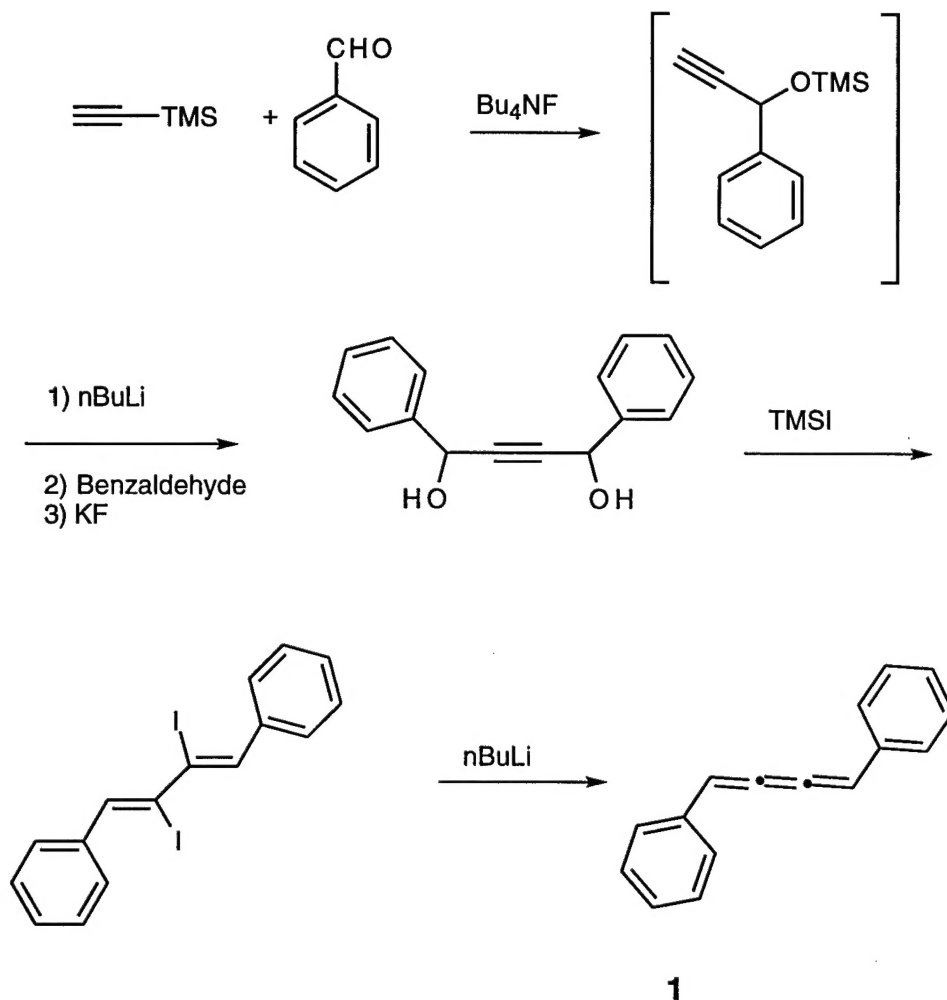
S. K. Pollack and A. Fiseha , Poly(2-butyne-1,4-diyl)s as Precursors to Novel Substituted Polyacetylenes in Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV., symposium held December 1-5, 1997, Boston, Massachusetts, U.S.A. Materials Research Society, Fall 1997 Meeting, Boston, MA, , J.R. Reynolds, A. K-Y. Jen, L.R. Dalton, M.F. Rubner and L.Y. Chang, Eds.,pp 725-732 (1998)

S. K. Pollack and A. Fiseha, A New Route to Soluble Poly(acetylene)s from Poly(butatriene)s, *ACS Polymer Preprints*, **39(1)**, 113, (1998).

The polymerization of simple butatrienes has long frustrated spectroscopists in their attempts to isolate and study the free monomeric molecule<sup>2-7</sup>. Carothers observed this phenomenon and obtained a patent on the potential use of butatriene as a reactive monomer, not understanding the nature of the polymer formed<sup>8</sup>. Recently, we have been studying the structure and potential applications of butatrienes as monomers in addition polymerization<sup>9-11</sup>. In reviewing of the literature concerning 1,2,3-butatriene, there were reports that in some situations, the normally white solid formed from its polymerization would convert to a yellow, blue or even black material<sup>2</sup>. This intrigued us as it implied the formation of a conjugated system. Based on our previous and ongoing studies, 1,2,3-butatrienes polymerize in the presence or absence of free-radical initiators via a 1,4-addition to produce a poly(2-butyne-1,4-diyl) structure.



For the case  $R=H$ , this creates a polymer which is formally  $(C_4H_4)_n$ . This is isomeric with the conjugated polymer poly(acetylene). We reasoned that the formation of colored materials could be due to rearrangement of the unconjugated, acetylene containing system to the thermodynamically more stable conjugated polyene. If one could design the butatriene monomer appropriately, such a rearrangement of the resulting substituted poly(2-butyne-1,4-diyl) could lead to conjugated polymers with unique electronic and physical properties. In this paper, we report on a first example of such a rearrangement .



## Experimental

Unless otherwise noted reagents were used as received. All solvents were purified using standard procedures. Melting points were obtained using a Fisher-Johns melting point apparatus and are reported uncorrected. Solution NMR data was obtained on a General Electric QE-300 FT-NMR system equipped with a Tecmag™ data system and were referenced either to an internal TMS standard or to solvent peaks. Infrared data were obtained using either a Perkin Elmer 1600 Fourier Transform Infrared spectrometer. Gel permeation chromatographic (GPC) analysis was carried out using a system consisting of a GBC Isocratic pump, a GBC UV/VIS detector, an Knauer refractive index detector and Rheodyne manual injector and a two Polymer Laboratories Plgel™ 3μm mixed bed C



Linear column (300 mm x 7.5 mm) interfaced to a data acquisition system of local design and calibrated with narrow molecular weight distribution polystyrene standards (Polymer Laboratories). Samples were eluted with toluene. ESR spectra were obtained both in the solid state and in solution in chloroform using a Bruker ER 2000-SRC spectrometer operating at 9.74 GHz at an RF power of 10 mW, modulation frequency of 100 KHz and a field modulation intensity 2.8 G. UV spectra were obtained using a Perkin Lambda 2 spectrometer. Fluorescence spectra were obtained using a Spex Fluorimax-2 spectrofluorimeter. In both cases, 1 cm quartz pathlength cells were used. DSC data was obtained on a Perkin-Elmer DSC 7 interfaced to a Pyrus Data station. All heating scans were conducted at 10°C/min. Heating and cooling was conducted under a nitrogen atmosphere. Hot-stage microscopy was performed using an Olympus BX-50 microscope equipped with a Linkham THMS 600 hot-stage and a LP92/LNP2 controller or a Instec HCS400 hot stage.

**Synthesis of 1,4-Diphenyl-2-butyne-1,4-diol<sup>1,2</sup>** Under a dry nitrogen atmosphere, 1.57 g (16 mmol) of trimethylsilylacetylene were added quickly to a stirred mixture of 1.24 g (11.6 mmol) of freshly distilled benzaldehyde and 0.208 g (0.8 mmol) of tetrabutylammonium fluoride in 25 mL of THF at -78°C. The cooling bath was removed after 5 minutes and the mixture was stirred at room temperature until all the benzaldehyde reacted (observation of the C=O band by IR). 7.2 mL (12 mmol) of 1.6M n-BuLi in hexane was added dropwise over 10 minutes followed immediately with 1.24 g (11.6 mmol) of benzaldehyde. After complete disappearance of benzaldehyde, 2.4 g of potassium fluoride in 25 mL of methanol was added and the mixture was stirred for 6 days. 50 mL of 5% w/v sodium bicarbonate was added and the product mixture was stirred for 15 minutes. The product was extracted several times with ether and the solvent was removed by rotary evaporator leaving a yellow oil. The product mixture was purified

by chromatography on silica gel using hexane/ethyl acetate as a solvent, giving a white solid (yield 25.2%). Mp: 142-144°C (lit<sup>3</sup> 143-144°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ ppm 2.16-3.29 (b, 2H, OH), 4.65, 5.5 (both s, diastereomeric CH, PhCH(OH)), 7-8 (m, 8.95H, PhCH(OH)); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm 64.6, 65.3 (PhCH(OH)C≡), 86.5 (PhCH(OH)C≡), 126.6, 126.9, 127.0, 128.2, 128.4, 128.6, 128.99, 140.4 (PhCH(OH)C≡); IR (thin film cast from CH<sub>2</sub>Cl<sub>2</sub>) 3446 (OH), 3055 (CH, aromatic), 2986 (CH stretch), 2306 (acetylene), 1600, 1492, 1450 (aromatic, characteristic), 1423 (CH bend) 1285 cm<sup>-1</sup> (CO) 749, 698 cm<sup>-1</sup> (mono-substituted benzene).

#### Synthesis of 2,3-Diiodo-1,4-diphenyl-4-butadiene<sup>4,5</sup>

To a solution of 1.82 g (12.9 mmol) of diphenylbutyndiol in 250 mL of dichloromethane was added a solution of 12.89 g (64.4 mmol) of iodotrimethylsilane in 20 mL of dichloromethane at -78°C over a period of 30 minutes, under nitrogen atmosphere. The mixture was stirred for 2 h at -78°C. A saturated solution of sodium bisulfite was added and the mixture was extracted with dichloromethane, dried over magnesium sulfate and the solvent was removed by rotary evaporator. The dark oily product was chromatographed on silica gel using hexane/ethyl acetate yielding a flaky greenish/yellow solid (yield 17.2%). Mp: 70-72°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm 6.95-7.0 (s, 2 H, PhCH=C(I)-), 7.2-7.51 (m, 10 H, PhCH=C(I)-); <sup>13</sup>C NMR(CDCl<sub>3</sub>) δ/ppm 99.4 (PhCH=C(I)-), 136.1 (PhCH=C(I)-), 128.3, 128.4, 141.4-141.7 (PhCH=C(I)-); IR (thin film cast from CCl<sub>4</sub>) 3050, 3021 (CH, aromatic), 1598, 1492, 1442 (aromatic, characteristic), 1557(-CH=CH(I)-) 749, 698 cm<sup>-1</sup> (mono-substituted benzene).

**Synthesis of Diphenylbutatriene (DPB, 1)** Under a dry nitrogen atmosphere, 2.0 mL (3.314 mmol) of 1.5 M *n*-BuLi in hexane was added to 1g (3 mmol) of diiododiphenylbutadiene in 30 mL of ether, at -78°C. The mixture was stirred for 2 h at -78°C, warmed up to -50°C and 5 mL of pentane was added and stirring continued for 10 minutes. The temperature was raised to -20°C and 1 mL of water was added. The product mixture was allowed to warm up to room temperature and dried with 1g of anhydrous magnesium sulfate and solvent was removed by rotary evaporator. The product (diphenylbutatriene) was purified (under nitrogen) over Florisil column using degassed hexane to give a low-melting solid (yield 91.9%). <sup>1</sup>H NMR δ/ppm 6.35-6.8 (s, 2 H, PhCH=C=), 7.13-7.62 ppm (m, 10 H, PhCH=C=). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm 109.5, 109.6, 109.7 (PhCH=C=), 125-127.8 and 136 (PhCH=C=, several peaks), 155 ppm(PhCH=C=); IR (thin film cast from CCl<sub>4</sub>) 3050, 3021(CH, aromatic), 1598, 1492, 1442 (aromatic, characteristic), 1943 1554 (-CH=C=C=CH) 748, 688 cm<sup>-1</sup> (mono-substituted benzene).

### **Synthesis of Poly(diphenylbutatriene) (2)**

Compound 1 (0.352 g, 1.81 mmol) was dissolved in 10 mL of THF and placed in a sealable vessel. The solution was degassed several times (freeze-pump-thaw, 6 cycles) and thermally polymerized at 120°C for 48 h. The homopolymer which was soluble in THF was precipitated from chloroform/methanol giving a light yellow precipitate. <sup>1</sup>H (CDCl<sub>3</sub>) NMR δ/ppm 6.35-6.80 (s, 2H,  $[-(Ph)CHC\equiv CCH(Ph)-]$ , 7.13-7.62 (m, 10 H,  $[-(Ph)CHC\equiv CCH(Ph)-]$ ; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm 45.4-45.9 (4 peaks,  $[-(Ph)CHC\equiv CCH(Ph)-]$ , 84.8, 84.4 ( $[-(Ph)CHC\equiv CCH(Ph)-]$ ).

(Ph)CHC≡CCH(Ph)-], 126.6, 128.7, 138.5, 138.7, 139.4,

-[-(Ph)CHC≡CCH(Ph)-],); IR (thin film cast from CH<sub>2</sub>Cl<sub>2</sub>) 3069, 3029 (CH, aromatic), 2246 (acetylene), 1600, 1492, 1450 (aromatic), 749, 698 cm<sup>-1</sup> (mono-substituted benzene); GPC molecular weight analysis :M<sub>w</sub>=14 kg mol<sup>-1</sup>, M<sub>n</sub>=8.7 kg mol<sup>-1</sup>, PD=1.6.

**Rearrangement of Poly(diphenylbutatriene) (2)<sup>6,7</sup>** Under a dry nitrogen atmosphere 60 mg of **2** in 50 mL of dry benzene was heated to 75°C. Upon addition of a few drops of saturated potassium *t*-butoxide in *t*-butanol, the light yellow solution turned brown and ca 8 mL of saturated potassium *t*-butoxide in *t*-butanol was added. The mixture was heated for 15 minutes and 25 mL of water was added. The product mixture was extracted with ether, washed several times with water to remove residual *t*-butanol and dried with anhydrous magnesium sulfate and solvent was removed by rotary evaporator leaving a dark brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm 7.13-7.62 (b,-(Ph)CH=CH-). <sup>13</sup>C NMR(CDCl<sub>3</sub>) δ/ppm 125-127.8 and 136 (-(Ph)CH=CH-, broad peaks). IR (thin film cast from CH<sub>2</sub>Cl<sub>2</sub>) 3069, 3029 (CH, aromatic), 1650 (C=C), 1600,1492,1450 (aromatic, characteristic), 749, 698 cm<sup>-1</sup>(mono-substituted benzene); GPC molecular weight analysis : M<sub>w</sub>=49 kg mol<sup>-1</sup>, M<sub>n</sub>=28 kg mol<sup>-1</sup>, PD=1.8.